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Understanding Fuel Cells on a Quantum Physics Level

Bent Sørensen
Roskilde University
Institute of Mathematics & Physics, Energy & Environment group
Universitetsvej 1, Bld. 27.2, DK-4000 Roskilde Denmark
boson@ruc.dk http://mmf.ruc.dk/energy

Abstract

A complete quantum mechanical description of the processes taking place at the positive and negative electrode catalyst of a hydrogen-oxygen fuel cell has been performed. The results demonstrate the importance of the charge state of the catalyst surface in determining the fuel cell reactions and notably the formation of water at the positive electrode. In an open circuit fuel cell, the water produced will accumulate on the catalyst surface, but when an external load is serviced, the surface charge diminishes and the water can leave the surface area. This type of calculation thus allows a better understanding of the requirements for water management, often identified as a key factor in improving fuel cell performance.

1. Introduction

The calculation models the catalyst surface as two layers of Ni, with surface reactions described by density functional theory (DFT) using the B3LYP potential and an SV basis [1]. The Ni lattice is expected to serve similarly to Pt catalyst layers, but DFT calculations are quicker and more reliable, due to the lower electron shells in play. Charge distributions are investigated by splitting the system into three subsystems each with prescribed charges, and estimating the total energy by use of the ONIOM technique [2]. The reason this is necessary is that the quantum system cannot from being given a total charge of say +4 (four protons released at the negative electrode and carried to the positive electrode) know that the entire charge initially is supposed to sit on the hydrogen atoms and subsequently by a number of intricate steps is distributed among the hydrogen and oxygen atoms and finally transferred to the underlying nickel surface. The calculations use a combination of restricted potential energy scans and local optimisations.

2. Positive electrode reactions

Preliminary [1] and very preliminary [3] calculations for the positive electrode reactions have been presented recently. Before that, only the dissociation of an oxygen molecule at a catalyst surface, and the corresponding hydrogen dissociation at the negative electrode catalyst, were successfully described on a quantum chemical level [4]. Attempts to describe quantum mechanically the following steps of water formation at the catalyst, followed by the water being able to leave the surface, have previously failed to reproduce all the processes as a spontaneous chain of reactions producing an electric current in an external circuit [3,5]. Both for the density functional model calculations and for the case of extending molecular dynamics models [6,7], the likely reason is the lack of sufficiently detailed treatment of charge distribution issues. This is illustrated by the calculations shown in Figure 1, using a density functional theory calculations with the PBEPBE potential and SV basis, but with only the overall charge specified. Calculated charge distributions are grossly incorrect and only the chemisorbed states (to the right in the figure) could be improved by adding larger chunks of the Ni lattice.

The present work describes the processes from receiving four protons from the negative electrode through the membrane (corresponding to the case of a PEMFC), then during their interaction with a dissociated oxygen molecule and finally to the formation of water after receiving four electrons from the positive electrode catalyst. The catalyst is still modelled as two

layers of Ni, and the surface reactions are described by density functional theory using the B3LYP potential and an SV basis [1]. However, where early calculations left it to the quantum chemical calculation to correctly distribute charges, the present work takes up the suggestion to use a splitting of the system into subsystems each with prescribed charge, and estimating the total energy by use of the ONIOM technique [2].

Furthermore, the general behaviour of the charge distribution near the catalyst surface is known (from experiments (such as [8]) to change as the current in the external circuit increases from zero (open circuit) to its maximum value. Therefore, the quantum calculation is repeated for total charges varying from +4 (because two water molecules are formed in the model) to zero, simulating increasing external currents.

The calculations used a combination of restricted potential energy scans and local optimisations. Figure 2 shows a favoured path of reactions with symmetry between the two OHH systems, showing the overall possibility of a spontaneous fuel cell reaction combining hydrogen and oxygen to water while building up a substantial electric potential for the external circuit power production. Similar behaviour is found for asymmetric cases, where one water molecule is formed and escapes before the other. The distribution of charges on atoms shown in Figure 3 illustrates the importance of charge distributions based on one model layer of ONIOM calculations, and includes asymmetrical reaction steps.

3. Negative electrode reactions.

The potential energy surface basis for dissociation of hydrogen molecules at a Ni catalyst surface was for the same lattice configuration as used here calculated in [1]. The corresponding 2-layer ONIOM calculation with the Ni lattice as the lower layer and two H-atoms as the upper layer gives rise to the selected potential energy values shown in Figure 4, for an overall charge starting at zero but increasing to +1, which allows one hydrogen ion to escape from the surface, while its electron has been transferred to the external circuit through the metal catalyst electrode. Expelling both H^+-ions in one step is found energetically less favoured. The preliminary ONIOM multilayer calculations presented here have a problem with keeping track of total spin, the conservation of which is not rigorously enforced by the program code, and it therefore may deviate from the correct one, sometimes causing absolute energies to be unreliable. This happens in Figure 4, when the spin of the included system components changes from zero to ½ However, the relative energies for similar configurations should still be reliable.

4. Concluding remarks

The calculations described were carried out on a small cluster of 3 GHz PC's and took several months of CPU time. Clearly the variations of variables had to be restricted, as even the 18 position variables of the 4H and 2O atoms (assuming the Ni-atom positions fixed) would require unrealistic computing times to produce just a crude potential energy surface based on say 10 values of each of the 18 parameters.

The study is clearly an ongoing one, with each series of calculations revealing new sides of the problem studied. The achievement to date gives a rudimentary understanding of the mechanism of fuel cell operation on a quantum mechanical level, which is certainly a novel accomplishment. Still, there are many limitations inherent in the necessarily approximate methods used, and assuring each result to be reliable requires a multitude of control calculations to be performed. For this reason the work has to be continued, with particular emphasis on the areas where the conclusions turned out particularly sensitive to details of assumptions made in carrying out the modelling.

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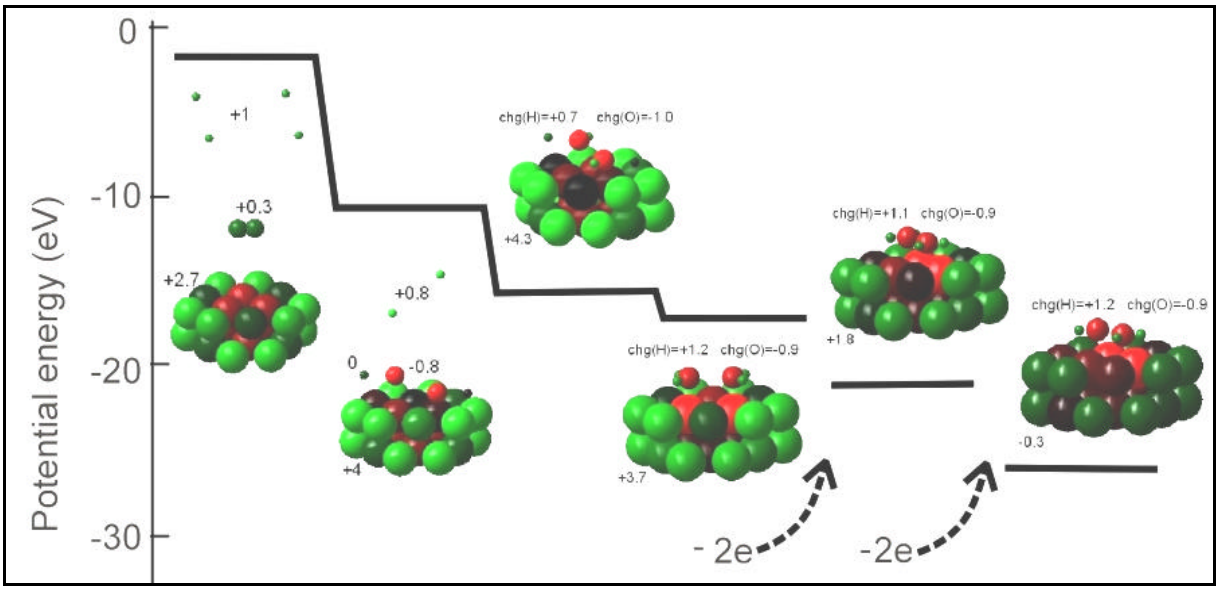

Figure 1. Early calculation of selected stages of hydrogen capture and water formation at the positive electrode of a PEM fuel cell. The four leftmost columns assumed a total charge of +4, while the rightmost columns assumed charges +2 and 0. This type of calculation fails to place the 4 charges on the hydrogen atoms in the leftmost column, but increasingly does better when the atoms come closer together. Yet the energy differences between steps are usually too large [3].

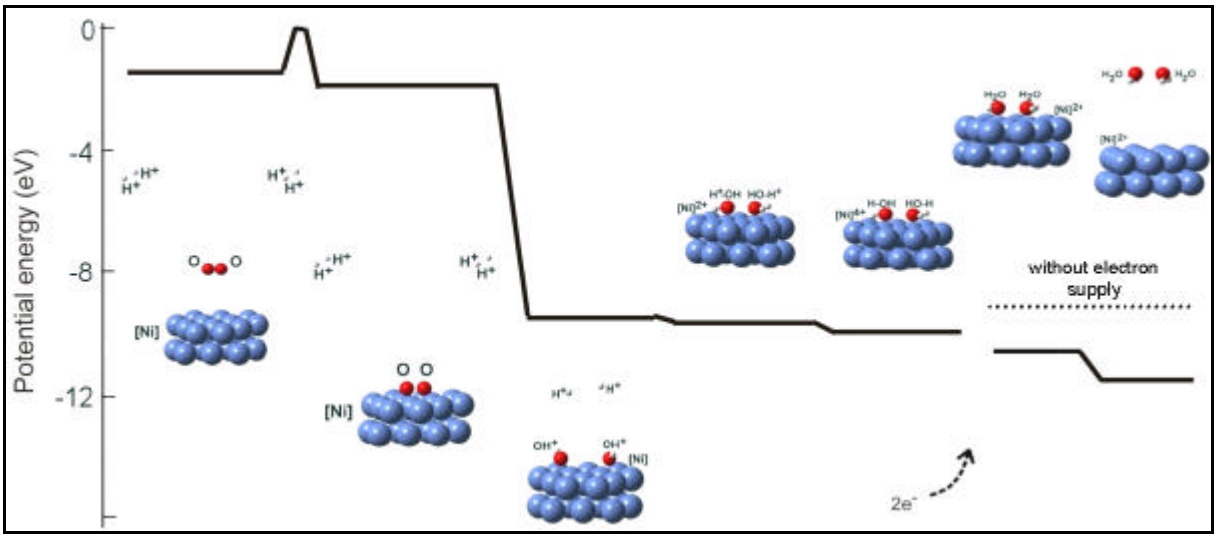

Figure 2. Selected stages en route to the formation and release of water at the positive electrode of a PEM fuel cell. The energy scale is adjusted for the binding energy of two additional electrons in the two rightmost columns. The calculated ΔE_{pot} from column 2 to column 3 considerably exceeds the experimental value [1].

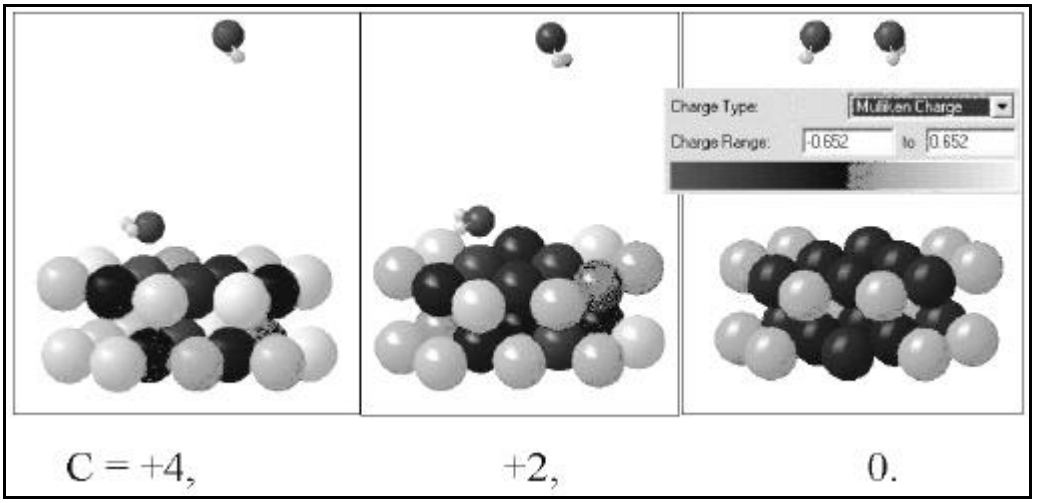

Figure 3. Atomic charge distribution for total charge varying from 4 (open circuit) to 0 (maximum current), as emerging from the lowest model layer of calculations similar to the ones shown in Figure 2.

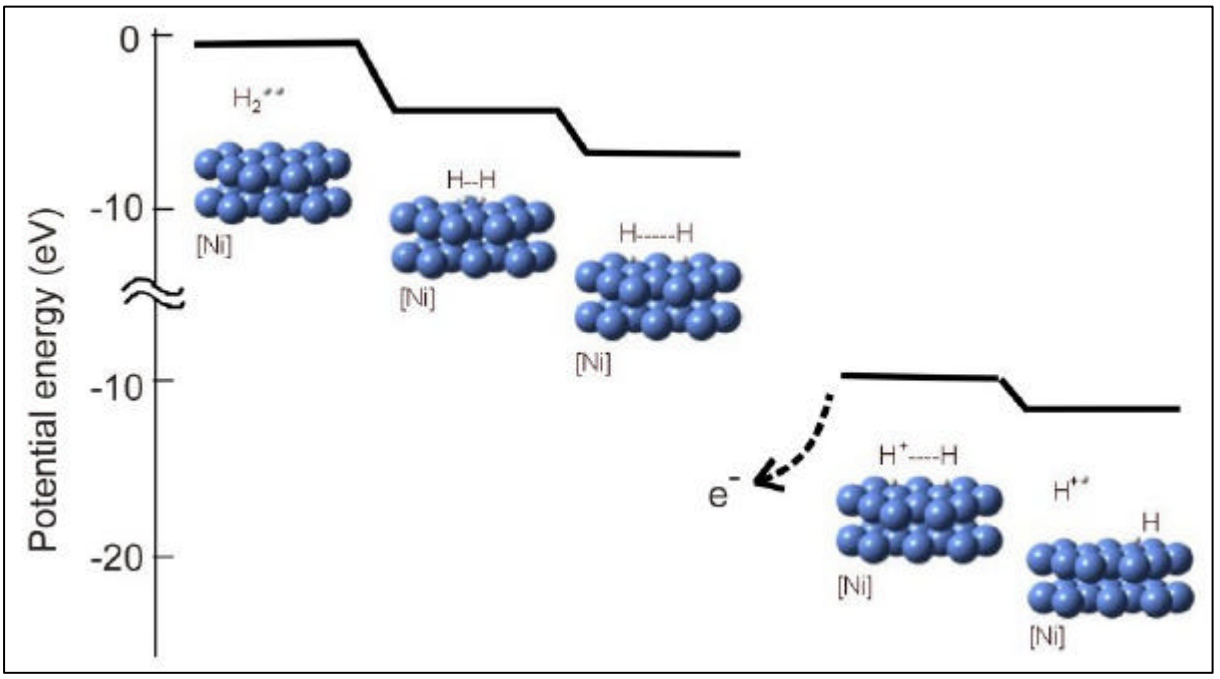

Figure 4. Selected stages en route to the hydrogen dissociation and hydrogen-ion release from the negative electrode of a PEM fuel cell. The energy scale is adjusted for the binding energy of one lost electron in the two rightmost columns, but due to spin change, the absolute energy change from column 3 to 4 cannot be calculated accurately with the ONIOM method.